Flame Retardant Exposure: Polybrominated Diphenyl Ethers in Blood from Swedish Workers

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Polybrominated diphenyl ethers (PBDEs) are used as additives in polymers and textiles to prohibit the development of fires. Because of the production and use of PBDEs, their lipophilic characteristics, and persistence, these compounds have become ubiquitous environmental contaminants. The aim of the present study was to determine potential exposures of PBDEs to clerks working full-time at computer screens and personnel at an electronics-dismantling plant, with hospital cleaners as a control group. Five PBDE congeners—2,2′,4,4′-tetraBDE; 2,2′,4,4′,5,5′-hexaBDE; 2,2′,4,4′,5,6′-hexaBDE; 2,2′,3,4,4′,5′,6-heptaBDE; and decaBDE—were quantified in blood serum from all three categories of workers. Subjects working at the dismantling plant showed significantly higher levels of all PBDE congeners in their serum as compared to the control group. Decabromodiphenyl ether is present in concentrations of 5 pmol/g lipid weight (lw) in the personnel dismantling electronics; these concentrations are comparable to the concentrations of 2,2′,4,4′-tetraBDE. The latter compound was the dominating PBDE congener in the clerks and cleaners. The major compound in personnel at the dismantling plant was 2,2′,3,4,4′,5′,6-heptaBDE. Concentrations of this PBDE congener are almost twice as high as for 2,2′,4,4′-tetraBDE in these workers and seventy times the level of this heptaBDE in cleaners. The total median PBDE concentrations in the serum from workers at the electronics-dismantling plant, clerks, and cleaners were 37, 7.3, and 5.4 pmol/g lw, respectively. The results show that decabromodiphenyl ether is bioavailable and that occupational exposure to PBDEs occurs at the electronics-dismantling plant. *Key words:* analysis, blood, contamination, DBDE, decabromodiphenyl ether, electronics recycling, flame retardants, levels, occupational exposure, PBDE, persistent organic pollutants, polybrominated diphenyl ethers. *Environ Health Perspect* 107:643–648 (1999). [Online 29 June 1999]
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Brominated flame retardants (BFR) comprise a large number of substance classes (*1*) including polybrominated diphenyl ethers (PBDEs) (*2*). PBDEs are used as flame retardants in plastics, textiles, coatings, and electrical components found in many common goods including computers, televisions, and electrical appliances (*2*). Technical PBDE products are manufactured as mixtures of penta-, octa- and decabromodiphenyl ethers, corresponding to the average bromine content. These products contain diphenyl ethers with mainly 4–6, 7–10, and 10 bromine atoms, respectively; e.g., 6 brominated diphenyl ethers (BDEs) of a total of at least 12 congeners are present at levels exceeding 1% by mass in a technical pentaBDE mixture, Bromkal 70-5DE (Chemische Fabrik Kalk, Cologne, Germany) (*3*). Globally, decaBDE is the most common PBDE, with a production of 30,000 metric tons/year. When the other PBDE products are included, total worldwide output is 40,000 metric tons/year (*4*).

After the discovery of PBDEs in pike from a river on the West Coast of Sweden in 1981 (*5*), numerous subsequent reports documented the ubiquitous distribution of PBDEs in the environment. PBDEs have been detected in sediments (*6–9*), wildlife,

and fish (*5,6,10–15*), and in human blood (*16*), mother's milk (*17–19*), and human adipose tissue (*20,21*). In biota, the dominating PBDE congener is 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) (*10–13,15,16,18,19*). Other examples of PBDE congeners reportedly present in the environment are 2,2′,4,4′,5-pentaBDE (BDE-99), 2,2′,4,4′,6-pentaBDE (BDE-100), 2,2′,4,4′,5,5′-hexaBDE (BDE-153), and 2,2′,4,4′,5,6′-hexaBDE (BDE-154) (*15,16,18,19*). [Individual PBDE congeners are numbered according to the numbering system of polychlorinated biphenyls (PCBs) (*22*).] Levels of BDE-47 in human blood and mother's milk are 2.9 and 4.7 pmol/g lipid weight (lw), respectively (*16,18*). For example, significantly higher concentrations have been reported in wild salmon (*Salmo salar*) from the Baltic Sea (620 pmol/g lw) (*15*) and in harbor seal blubber, where up to 2,500 pmol/g has been reported (*13*). Despite the fact that human PBDE concentrations are still significantly lower than those of PCB and DDE in mother's milk, a dramatic increase in PBDE concentration in milk from Sweden has been reported, corresponding to a redoubling every 5 years (*18*). Only a few scientific articles have so far reported on decaBDE (BDE-209) as an

environmental contaminant. For example, BDE-209 has been determined in water and sediments (*9*) and in human adipose tissue (*21*). The presence of hexaBDE to nonaBDE were also reported in the latter study, but neither structure identifications nor any quantifications were made. Quantitative measurements of PBDEs in ambient air at the plant for dismantling electronics, from which the personnel were sampled for the present study, show concentrations of BDE-183 and BDE-209 in the range of 6.3–87 and 12–200 ng/m^3, respectively, whereas the BDE-47 concentrations were 1.2–2.1 ng/m^3 (*23*). BDE-47 was not detected in the air at ordinary offices, whereas BDE-183 and BDE-209 were detected at levels of at most 0.08 ng/m^3.

Although PBDEs seem to have low toxicity in many tests (*2*), recent data indicate that they may be more harmful than previously expected. Several PBDE congeners interfere with the aryl hydrocarbon (Ah) receptor (*24*). BDE-99 induces learning disabilities in mice (*25*) analogous to those caused by 2,2′,5,5′-tetrachlorobiphenyl (CB-52), one of the most potent PCB congeners eliciting this effect (*26*). BDE-47 is transformed in rats and mice to hydroxylated metabolites (*27*) that compete with thyroxin for the binding site on transthyretin (*28*). Some hydroxy-PBDEs also reportedly bind to the thyroid receptor (*29*). Taken together, these observations indicate that PBDEs might act as endocrine disruptors.

Generally, humans are most probably exposed to PBDEs through similar exposure routes as many neutral lipophilic organohalogen compounds such as PCB congeners and DDT-related compounds, with food as the major source (15,30). Inhalation of particulate-bound PBDEs in certain occupational settings may, however, also contribute to human exposure, whereas gaseous phase exposure to PBDEs probably is of minor importance because of the low vapor pressures of these compounds (2). The aim of the present study was to determine if occupational exposure can be related to PBDE body burdens, and if so to quantify them. Serum samples were collected and analyzed from three groups: subjects employed in an electronics-dismantling plant, clerks working full-time at computer screens, and, as a control group, hospital cleaners. The study includes methodological development for the analysis and quantification of BDE-209 in human serum.

Materials and Methods

Chemicals. Synthesized reference compounds used for preparation of standards and their origin are given in Table 1. 2,2′,3,4,4′,5′,6-Heptabromodiphenyl ether (BDE-183) was synthesized by bromination of diphenyl ether at room temperature in the presence of iron filings. According to gas chromatography (GC) analysis, the final product consisted of BDE-183 (82%) and BDE-153 (18%). The identity of BDE-183 was determined by ^{1}H nuclear magnetic resonance (NMR) and comparison with the spectrum recorded for the authentic BDE-153 (31,32). ^{1}H NMR (270 MHz, $CDCl_3$) for BDE-183 was δ 7.97 (s, H3), 7.89 (s, H3′), 6.57 (s, H6′); for BDE-153 it was δ 7.90 (s, H3), 7.08 (s, H6). Decabromodiphenyl ether (97%) was obtained from LabKemi (Stockholm, Sweden). A commercial octaBDE product, Bromkal 79-8DE (Bk79-8; Chemische Fabrik Kalk) was used as a qualitative standard. 2,3,3′,4,4′,5,5′-Heptachlorobiphenyl (CB-189) (33) and 2,2′,3,3′,4,4′-hexabromodiphenyl ether (BDE-128) were used as internal standards for quantification of CB-153 and PBDEs, respectively. *n*-Hexane, distol grade, was from Fisher Scientific (Leicestershire, UK); methyl *tert*-butyl ether (MTBE), HPLC grade, was from Rathburn chemicals (Walkerburn, Scotland), and 2-propanol, *p.a.* grade, was from Prolabo (Cedex, France). Silica gel 60 (0.063–0.200 mm), sulfuric acid, and hydrochloric acid, *p.a.* grade, were from Merck (Darmstadt, Germany) and potassium hydroxide, *p.a.*, was from Eka Nobel (Bohus, Sweden).

Instruments. A Varian 3400 gas chromatograph, equipped with a DB-5 capillary column (30 m × 0.25 mm i.d., 0.25-µm film thickness; J&W Scientific, Folsom,

CA) and an electron capture detector (ECD) was used. Hydrogen was used as carrier gas and nitrogen as make-up gas. Injections were made in the splitless mode. The column oven temperature was programmed as 80°C (2 min), 10°C/min, to 300°C (6 min). The injector and detector temperatures were 250 and 360°C, respectively. Data were collected and processed with a personal-computer-based ELDSPro v1.0 data system (Chromatographic Data System AB, Stockholm, Sweden).

GC/mass spectrometry (MS) was performed on a Finnigan TSQ 700 instrument (ThermoQuest, Bremen, Germany). A DB-5HT capillary column (15 m × 0.25 mm i.d., 0.1-µm film thickness; J&W Scientific) with helium as the carrier gas (head pressure 3 psi) was used. Splitless injections were made at an injector temperature of 260°C. The column oven temperature was programmed as 80°C (1 min), 15°C/min, to 300°C (10 min). The ion source temperature was 200°C and the pressure 6.5 torr. PBDEs were quantified using bromide ions formed by dissociative electron-capture reactions with a primary electron energy of 70 eV. Selected ion monitoring (SIM) was carried out for both bromide isotopes, *m/z* 7′ and 81 (34). Methane 4.5 (AGA, Stockholm, Sweden) of ≥ 99.995% purity and with ≤ 5 ppm O_2 was used as the electron thermalization buffer gas. On-column injections were made for GC/MS quantification of BDE-209 using a septum-equipped programmable injector fitted with a high-performance insert. The injector temperature was programmed as 60°C, 180°C/min, to 320°C. The oven temperature was programmed as 80°C (1 min), 15°C/min, to 300°C (16 min). All other GC and MS parameters were similar to those described above. Typical SIM chromatograms of higher brominated (≥ 7 bromine atoms) diphenyl ethers (*m/z* = 79 and 81) are shown in Figure 1.

^{1}H NMR spectra were recorded in $CDCl_3$ solutions with a JEOL EX270 270 MHz instrument (JEOL, Akishima, Japan) at room temperature.

Blood sampling and interview. Three occupational groups were studied. One group consisted of 15 adult males and 4 females working at an electronics-dismantling plant. Their work included manual dismantling of electronic goods such as personal computers, television sets, and radios. Plastic goods were ground using a shredder. The personnel in charge of the shredder wore dust protection masks made of filter paper during this work; no respiratory protection was used for other work tasks. The second group consisted of 20 female clerks working full-time in front of computer screens for almost 8 hr/day. The third group consisted of 20 female hospital cleaners. For all subjects, venous blood was drawn from a cubital vein into evacuated plain tubes (Vacutainer, Rutherford, NJ). The serum was centrifuged and thereafter transferred to acetone-washed glass bottles. The serum samples were coded, frozen, and kept at -20°C until chemical analysis. At the time of sampling, all subjects underwent an interview about their dietary habits. The electronics-dismantling workers were questioned about specific work tasks. The age distribution, employment time, and amount of fish consumption of all study subjects are given in Table 2. Blood samples from the electronics-dismantling workers were drawn immediately before their summer vacation, and a new blood sample was drawn from 11 of them immediately before they resumed work. The median occupational exposure free period (i.e., holiday) between the blood samples was 28 days (range 21–35).

Informed consent was obtained from all participating subjects. The study was approved by the Ethics Committee of Lund University (Lund, Sweden).

Table 1. Structures of the PBDE standards used, recovery data, and methods for their synthesis.

| BDE No.[a] | Structure | Recovery (%) | | | | Reference[b] |
| | | High dose | | Low dose | | |
		Average	SD	Average	SD	
47	2,2′,4,4′	78	4	69	4	(31)
77	3,3′,4,4′	91	7	86	4	(32)
85	2,2′,3,4,4′	77	10	84	5	(31)
99	2,2′,4,4′,5	95	6	94	9	(31)
100	2,2′,4,4′,6	104	4	98	4	(32)
128 (IS-2)	2,2′,3,3′,4,4′	82	14	104	7	(31)
138 (IS-1)	2,2′,3,4,4′,5′	81	10	94	4	(31)
153	2,2′,4,4′,5,5′	82	8	95	4	(31)
154	2,2′,4,4′,5,6′	82	9	86	4	(32)
183	2,2′,3,4,4′,5′,6	91	1	95	3	c
209	2,2′,3,3′,4,4′,5,5′,6,6′	101	8	93	11	c

Abbreviations: BDE, brominated diphenyl ether; IS-1 and IS-2, internal standards; SD, standard deviation.
[a]The polybrominated diphenyl ethers have been given numbers according to the numbering of polychlorinated biphenyls (22). [b]To method for synthesis. [c]See "Chemicals" section.

Sample clean-up and analysis. The serum extraction procedure used has been fully described elsewhere (*35*). Briefly, hydrochloric acid (6 M, 1 mL), 2-propanol (6 mL), and the internal standards CB-189 (3 ng) and BDE-128 (0.1 ng) were added to the serum samples (5 g). The samples were extracted twice with hexane/MTBE (1:1). The organic phase was washed with potassium chloride in water (1%). The solvent was evaporated and the lipid content gravimetrically determined for each sample. The extracts were dissolved in hexane and neutral compounds were isolated from acidic substances by partitioning with potassium hydroxide (0.5 M potassium hydroxide in 50% ethanol). The neutral fraction containing PBDEs was treated with concentrated sulfuric acid (2 mL) and subsequently eluted with hexane through a silica gel/sulfuric acid column [2:1 w/w (0.5 g)] prior to GC (ECD) and GC/MS electron capture negative ionization (ECNI) analysis.

Identification and quantification. A PBDE standard mixture containing the PBDE congeners listed in Table 1 was added to one of the samples from the group at the dismantling plant to verify the identity of the PBDE congeners present. A technical octaBDE mixture (Bromkal 79-8DE) was used to verify the presence of higher PBDE congeners in the serum samples. Quantification of the PBDE congeners was made using authentic PBDE standards, as given in Table 1, prepared at five concentrations. The quantifications of the PBDEs were made in relation to the calibration curves obtained by GC/MS. Quantification of CB-153 was performed by GC (ECD) using single-point calibration. Blank samples ($n = 4$) were analyzed in parallel to the serum samples. Quantifications of BDE-47, BDE-153, BDE-154, and BDE-183 were only done if the concentration of the analyte was at least twice the blank sample level. For these PBDE congeners, the limit of quantification (LOQ) was thus directly related to the blank sample levels of each compound. The signal to noise (S/N) ratio was used to determine limit of detection (LOD) and LOQ for BDE-209 because this compound was only detectable in one of four blank samples. S/N ratios were calculated by ICIS2 software (ThermoQuest), for the GC/MS instrument used, after comparison with those measured manually. The LOD and LOQ for BDE-209 were 0.3 and 0.7 pmol/g lw, respectively.

Recovery experiment. Determination of target recovery was made by quantification of the PBDE congeners given in Table 1 added to serum at low (0.03 ng/g serum) and high (0.2 ng/g serum) concentrations. Four replicate samples were analyzed at each concentration. PBDE recoveries from the low and high spike trials range from 69 to 104% and 77 to 104%, respectively (Table 1).

Statistical methods. The Mann-Whitney U-test was used to test group differences for
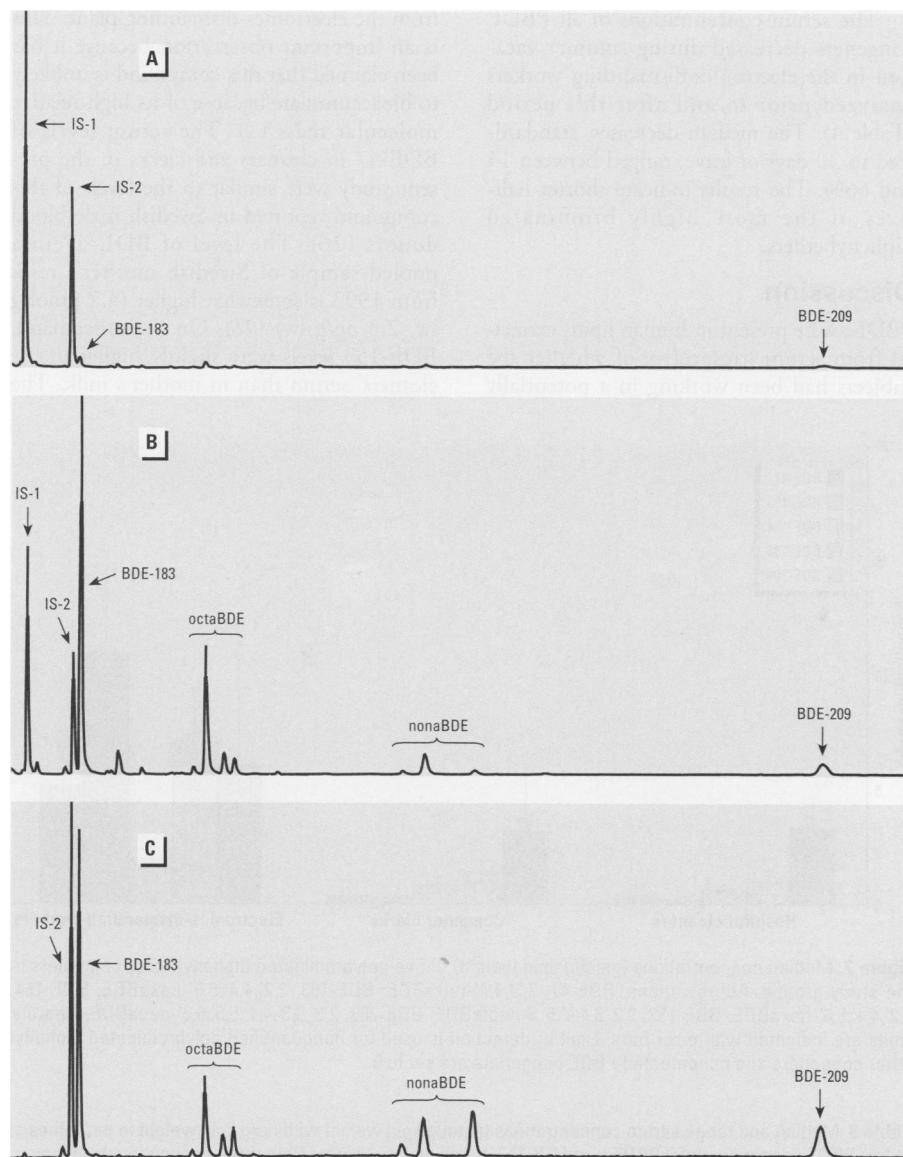
Figure 1. Typical selected ion mass chromatographs (SIM) of bromide ion isotopes (*m/z* 79 and 81) from (*A*) a female hospital cleaner and (*B*) a female worker at an electronics-recycling plant for PBDEs with 7–10 bromine substituents. (*C*) For comparison, a SIM is shown for a commercial octaBDE product, Bromkal 79-8DE (Chemische Fabrik Kalk, Cologne, Germany). Abbreviations: BDE-183, 2,2',3,4,4',5',6-heptaBDE; BDE-209, 2,2',3,3',4,4',5,5',6,6'-decaBDE. All identified peaks are labeled. The internal standard was BDE-128 (IS-2) and the injection spike was BDE-138 (IS-1).

Table 2. Occupation, age, employment time, and fish consumption among study subjects.

| Occupational groups | Subjects (no.) | | | Employment (years) | | Age (years) | | Fish consumption (meals/month) | | | |
| | | | | | | | | Fatty fish (Baltic Sea) | | Total | |
	Females	Males	Total	Median	Range	Median	Range	Median	Range	Median	Range
Hospital cleaners	20	0	20	16	2–30	48	30–60	0	0–3	4	0–8
Computer clerks	20	0	20	17	4–37	54	25–61	0	0–0	4	0–10
Electronics dismantlers	4	15	19	2	0.04–5	46	25–60	1	0–4	4	0–6

continuous variables. The Spearman rank order correlation test was used to assess correlations. Statistical significance corresponds to $p \leq 0.05$.

Results

The PBDE congeners shown in Figure 2 were detected in all blood samples analyzed, except for BDE-209, which was detected in 45 of 59 samples. The levels and patterns, however, were different between the study groups (Figures 1 and 2). The two pentaBDEs, BDE-99 and BDE-100, were present in all samples but are not shown in Figure 2 because these peaks were chromatographically disturbed. Accordingly, data on these PBDE congeners were excluded because it was not possible to accurately quantify them. Typical ECNI-MS chromatograms for heptaBDE–decaBDE are shown in Figure 1, representing a female hospital cleaner and a female worker from the electronics-dismantling facility. For comparison, the SIM trace of a commercial octaBDE product, Bromkal 79-8DE, is also shown in Figure 1. Clusters of octaBDEs and nonaBDEs were confirmed to be present in the blood samples of the electronics-dismantling workers but no quantitative measurements were performed because of the lack of authentic standards. However, higher relative concentrations, as shown in the chromatograms of the octaBDEs and nonaBDEs (Figure 1), were determined in serum from the personnel at the electronics-dismantling plant as compared to those with other occupations.

For the three occupational groups, the concentrations (pmol/g lw) of BDE-47, BDE-153, BDE-154, BDE-183, BDE-209, and the sum concentrations of these PBDE congeners, as well as of CB-153, are given in Table 3. BDE-209 was detected in 14 of 20 cleaners and in 13 of 20 clerks but was above the LOQ (0.7 ng/g lw) in 7 cleaners and 6 clerks. It was possible to quantify BDE-209 in all but two of the subjects working at the dismantling plant prior to their vacation. The electronics-dismantling workers had significantly higher plasma levels than the cleaners of all measured organohalogen compounds. The relative increase was most pronounced for BDE-183 (approximately 70 times the median value), whereas the corresponding values for the other compounds varied between two and seven times. For the computer clerks, small but significantly elevated levels were observed for three of the compounds (BDE-153, BDE-154, and BDE-183) as compared to the cleaners.

Clear correlations between CB-153 and age were observed in both hospital cleaners ($r_s = 0.51$, $p = 0.02$) and the personnel at the

dismantling plant ($r_s = 0.70$, $p < 0.001$). The consumption of fish was low in the studied groups and no significant correlations were found between CB-153 and total consumption of fish or fatty fish from the Baltic Sea. BDE-47, BDE-183, and BDE-209 concentrations did not correlate with age or fish intake (data not shown).

The serum concentrations of all PBDE congeners decreased during summer vacation in the electronics-dismantling workers analyzed prior to and after this period (Table 4). The median decreases, standardized to 30 days of leave, ranged between 14 and 66%. The results indicate shorter half-lives of the more highly brominated diphenyl ethers.

Discussion

PBDEs were present in human lipids extracted from serum irrespective of whether the subjects had been working in a potentially

non-PBDE contaminated environment or not. The results clearly show that PBDEs are environmental contaminants of concern not only for wildlife (10–13,15,16,18,19) but also for humans. However, the PCB levels were still higher than the PBDE levels.

Interestingly, BDE-209 was present in cleaners and clerks as well as in workers from the electronics-dismantling plant. This is an important observation because it has been claimed that this compound is unlikely to bioaccumulate because of its high relative molecular mass (2). The serum levels of BDE-47 in cleaners and clerks in the present study were similar to the levels of this compound reported in Swedish male blood donors (16). The level of BDE-47 in a pooled sample of Swedish mother's milk from 1997 is somewhat higher (4.7 pmol/g lw, 2.3 ng/g lw) (18). On the other hand, BDE-153 levels were slightly higher in the cleaners' serum than in mother's milk. The
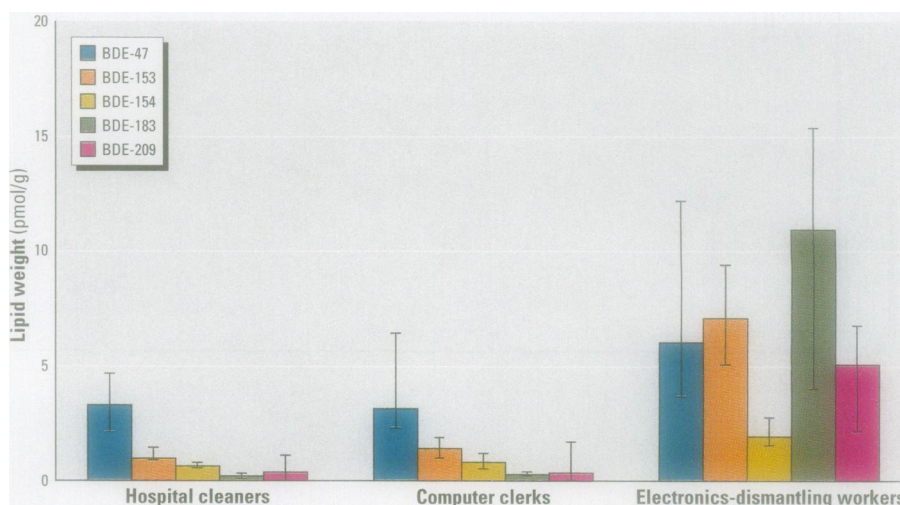
Figure 2. Median concentrations (pmol/g lipid weight) of five polybrominated diphenyl ether congeners in the study groups. Abbreviations: BDE-47, 2,2',4,4'-tetraBDE; BDE-153, 2,2',4,4',5,5'-hexaBDE; BDE-154, 2,2',4,4',5,6'-hexaBDE; BDE-183, 2,2',3,4,4',5',6-heptaBDE; BDE-209, 2,2',3,3',4,4',5,5',6,6'-decaBDE. Quartile limits are indicated with error bars. Limit of detection is used for nonquantified polybrominated diphenyl ether congeners and nondetected PBDE congeners are set to 0.

Table 3. Median and range serum concentrations (pmol/g lipid weight with ng/g lipid weight in parenthesis) of five PBDE congeners, total PBDEs, and CB-153 are given for subjects from three occupational settings.

Compound	Hospital cleaners (n = 20)		Computer clerks (n = 20)			Electronics dismantlers (n = 19)		
	Median[a]	Range[a]	Median[a]	Range[a]	p[b]	Median[a]	Range[a]	p[b]
BDE-47	3.2 (1.6)	< 1–34	3.0 (1.5)	< 1–10	> 0.5	5.9 (2.9)	< 1–47	0.02
BDE-153	0.89 (0.57)	0.64–7.6	1.3 (0.85)	0.80–5.1	0.02	7.0 (4.5)	3.2–19	< 0.001
BDE-154	0.59 (0.38)	0.25–1.4	0.79 (0.51)	0.43–1.5	0.04	1.9 (1.2)	0.74–7.4	< 0.001
BDE-183	0.16 (0.12)	0.025–0.39	0.24 (0.18)	< 0.02–1.4	0.02	11 (7.8)	3.1–26	< 0.001
BDE-209	< 0.7 (< 0.7)	< 0.3–3.9	< 0.7 (< 0.7)	< 0.3–8.0	> 0.5	5.0 (4.8)	< 0.3–9.9	< 0.001
sPBDE[c]	5.4 (3.3)	3.1–39	7.1 (4.1)	3.9–17	0.1	37 (26)	15–75	< 0.001
CB-153	330 (120)	120–1,000	480 (170)	130–1,300	0.08	760 (270)	190–2,200	< 0.001

Abbreviations: BDE-47, 2,2',4,4'-tetraBDE; BDE-153, 2,2',4,4',5,5'-hexaBDE; BDE-154, 2,2',4,4',5,6'-hexaBDE; BDE-183, 2,2',3,4,4',5',6-heptaBDE; BDE-209, 2,2',3,3',4,4',5,5',6,6'-decaBDE; CB-153, 2,2',4,4',5,5'-hexaCB; PBDE, polybrominated diphenyl ethers.
[a]Amount present in blank samples subtracted. [b]Level of significance derived from Mann-Whitney U-test hospital cleaners as control. [c]Sum of the PBDE congeners quantified, using values obtained for limit of quantification and detection for nonquantified samples.

clerks show slightly but significantly higher levels of BDE-153, BDE-154, and BDE-183, whereas no statistical difference was observed for BDE-47 and BDE-209 (Table 3). This is an indication that computer work may cause exposure to PBDEs. However, the plasma levels among both cleaners and clerks range up to one order of magnitude for all the PBDE congeners. This also indicates that other exposure sources, e.g., the diet, are important for the individual exposure. Additional work is necessary to confirm the observation that clerks working at computer screens may be occupationally exposed to PBDEs. Higher concentrations of CB-153 than of PBDEs were observed in the cleaners and clerks. This major PCB congener is strongly correlated to the total PCB level in serum (36). For comparison, slightly lower CB-153 levels were found in plasma from 40 men (16) as compared to the female cleaners and clerks. These levels were similar to the relative difference in BDE-47 levels between these two study groups (compare above). The similarities in the PBDE congener pattern between cleaners and clerks might indicate that the exposure routes are similar.

Significantly higher concentrations of each of the individual PBDE congeners analyzed were found in the personnel working at the electronics-dismantling plant as compared to the levels in cleaners and clerks (Table 3, Figure 2). Particularly high concentrations of BDE-183 were found—70 times that of the control group on a molar basis—whereas the smallest difference as compared to the control group was observed for BDE-47 (1.8 times). In addition, the CB-153 to BDE-183 ratio is significantly lower in the serum of the workers at the dismantling plant (approximately 70) as compared to that of the cleaners and clerks (approximately 2,000). The workers at the dismantling plant also had high levels of

octaBDEs and nonaBDEs, as shown in a representative chromatogram of the serum sample from a female worker (Figure 1B). This shows that electronics-dismantling work results in exposure to higher brominated PBDEs as compared to hospital cleaning or full-time work at a computer monitor. It is reasonable to believe that the personnel dismantling electronics are exposed to higher concentrations of heptaBDE to decaBDE, which are present as BFR in the goods taken in for recycling. In fact, high levels of particle-bound BDE-183 and BDE-209 have been determined in the ambient air at the dismantling plant (23).

It must be emphasized that BDE-209 is present in almost all the serum samples. This shows that even a molecule with a high molecular mass, such as BDE-209, is bioavailable. An implication of this observation is that more effort must be made to determine the concentrations of this compound in environmental samples, a need that is further supported by the high volume production of decaBDE (30,000 metric tons/year) (2,4). Authentic standards of heptaBDE–nonaBDE (not yet available) will be required for both identification and quantification of these higher brominated diphenyl ethers.

It is evident that occupational exposure to PBDE occurs at the plant for dismantling of electronics. This is strengthened by the different levels of the PBDE congeners quantified prior to and after the vacation of 11 of the workers at the plant (Table 4). Interestingly, there seem to be different half-lives depending on bromination degree of the diphenyl ethers; the more bromine in the molecule, the shorter half-life. However, the kinetics data in this study must be confirmed. The observation that the higher brominated congeners have a shorter half-life is consistent with reported data on metabolic rate of the two PBDE congeners BDE-47 and BDE-209. BDE-47 metabolism was studied in the rat and the mouse, and was well absorbed but slowly metabolized, forming hydroxylated metabolites that were excreted mainly via feces (27). BDE-209 was poorly absorbed and rapidly excreted after an oral dose; after i.v. administration the compound was also rapidly eliminated from the rat, partly as metabolites (37). Actual half-lives were not calculated in either of the two studies, but the data support the observation in the present study that BDE-209 is more rapidly eliminated than the lower brominated PBDEs. Further studies on the kinetics of these compounds are needed to clarify the bioaccumulation at exposure for brominated flame retardants.

Because PBDEs are present in food items, e.g., fish (8,15) and wildlife (12), it is reasonable to believe that dietary intake plays an important role in the external exposure of

these persistent compounds in humans. Inhalation may be a reason for the low but still significantly increased ($p = 0.02$) levels of BDE-183 in the clerks working at terminal screens as compared to cleaners. The exposure routes are partly different for BDE-47 and BDE-183, i.e., that food is a more important source for BDE-47 because it is the major contaminant in wildlife (compare above), whereas airborne uptake seems more pronounced for BDE-183. Airborne exposure, via inhalation of BDE-183, BDE-209, and octaBDEs–nonaBDE, is evident from the results in personnel working at the electronics-recycling plant. However, BDE-209 is present in higher levels than BDE-183 in the air at the dismantling plant (23). The observed higher levels of BDE-183 in serum might thus be due to a more rapid turnover of BDE-209 than of BDE-183 or better bioavailability of the heptabrominated than the decabrominated diphenyl ether. It is currently not possible to verify mechanisms of uptake and elimination of BDE-209 or BDE-183 in the electronics-dismantling workers. Further, no correlations were observed for any of the PBDE congeners with age or fish consumption. This is not unexpected because the occupational exposure may have obscured the influence of other sources of intake.

This work includes methodological development for analysis of the highest brominated diphenyl ethers, e.g., BDE-209, nonaBDEs, and octaBDEs. It is important to be able to quantify BDE-209 because this is a major BFR product (2,4). BDE-209 is efficiently extracted by the method used (35) but it was necessary to use an alternative GC method to improve the analysis. Hence, the quantification of BDE-209 was performed by MS (ECNI) after on-column injections and analyte separation on a short (15 m) GC column.

The present work shows that exposure to BFR not only occurs by consumption of contaminated food but also via inhalation of airborne particulate matter. PBDEs are persistent bioaccumulating substances with lipophilic characteristics and unfavorable biologic effects (24,25). Further studies need to be performed to gather better data on both background and occupational exposure to PBDEs. Finally, the results obtained call for detailed studies on the kinetics of PBDEs to improve the risk assessment of this class of environmental contaminants.

Table 4. Median and range of decrease (percentage) in serum concentrations of quantified polybrominated diphenyl ether congeners during exposure-free vacation, standardized to a 30-day period for electronics-dismantling workers.

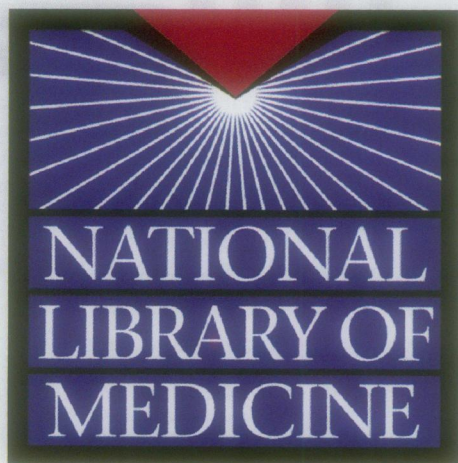| Compound	n	Median	Range
BDE-47	9[a]	-14	-39 to 3.5
BDE-153	11	-14	-38 to -2.1
BDE-154	11	-14	-42 to 6.7
BDE-183	11	-30	-52 to -7.9
BDE-209	5[b]	-66	-100 to -47

Abbreviations: BDE-47, 2,2',4,4'-tetraBDE; BDE-153, 2,2',4,4',5,5'-hexaBDE; BDE-154, 2,2',4,4',5,6'-hexaBDE; BDE-183, 2,2',3,4,4',5',6-heptaBDE; BDE-209, 2,2',3,3',4,4',5,5',6,6'-decaBDE.
[a]For two subjects the BDE-47 levels were below the limit of quantification. [b]For five workers the BDE-209 levels were below the limit of quantification after their vacations and one outlier was excluded.

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